[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE COLLEGE]

Hydrogen Fluoride as a Condensing Agent. IV. The Reaction of Cyclopropane with Benzene

BY J. H. SIMONS, S. ARCHER AND ELIZABETH ADAMS

In the two previous papers in this series[1] it was shown that hydrogen fluoride was an efficient agent to promote the reaction between either olefins and aliphatic halides and aromatic compounds.

Of considerable interest is the reaction of cyclopropane and benzene. Ipatieff and Grosse[2] carried out this reaction using aluminum chloride and found that only the normal propylbenzenes were formed. We have used hydrogen fluoride to cause the same reaction and have found a similar result, *i. e.*, the normal compound is the only product.

It is believed that cyclopropane does not isomerize to form propylene before alkylation.[2] A possible mechanism to account for the formation of the normal rather than the iso compound may be given. The cyclopropane molecule, being under strain, will be the center of an abnormal electromagnetic field, as is indicated by its magnetic susceptibility.[3] This may cause it to add a proton to form a hypothetical and transitory propyl ion. The additional strain may cause the ring to break and irrespective of where it breaks a normal propyl positive ion will be formed. The reaction of this ion with benzene will produce normal propylbenzene and a proton.

In the reaction between paraffins and olefins catalyzed by boron trifluoride with hydrogen fluoride as a promoter, Grosse and Linn[4] assumed that the initial step in the mechanism was the addition of the acid to the double bond, followed by the removal of hydrogen fluoride as the alkyl fluoride condensed with the saturated hydrocarbon. A similar mechanism may be postulated for the reaction between olefins and aromatics, as catalyzed by hydrogen fluoride. However, the suggested course of reaction does not adequately explain the reactions of cyclopropane. When this hydrocarbon reacts with hydrogen fluoride, *n*-propyl fluoride is predominantly formed, along with a small but significant amount of isopropyl fluoride. If it is the alkyl fluoride that reacts with the aromatic hydrocarbon, then one should expect both the normal and the iso compound to be formed when cyclopropane reacts with benzene. Yet it has been shown that no isopropylbenzenes are found in the reaction products. It is therefore assumed that the organic reactions catalyzed by hydrogen fluoride proceed through some ionic mechanism similar to those postulated by Whitmore for polymerizations and rearrangements.

Experimental

Sulfonamide Method of Identification.—In order to evaluate the composition of a possible mixture of normal and isopropylbenzene, a method employing the melting points of the sulfonamide derivatives was employed.

The sulfonamides were usually prepared in triplicate. A 3-g. sample was shaken with twice its volume of concd. sulfuric acid until the hydrocarbon dissolved completely. A saturated salt solution was added to precipitate the sulfonic acid and the latter was washed free of sulfuric acid with more of the salt solution. After drying at 110°, the sulfonic acid was treated with 8 to 10 g. of phosphorus pentachloride; and the mixture was then heated on the steam-bath for four hours. At the end of this time, the mass was poured into water, extracted with ether, washed with water and dried over sodium sulfate. Ammonia was passed onto the sulfonyl chloride for one hour. The ammonium chloride was filtered off and the solution dried again over sodium sulfate. The ether was evaporated and a melting point taken without recrystallization: m. p. of *n*-propyl sulfonamide, 102.5°; m. p. of isopropyl sulfonamide, 98°; m. p. of 57:43 mixture of iso and normal, respectively, 73°. The latter was the lowest point on the melting point curve. Mixtures of varying percentages of each were made and the melting points taken. From the data, a temperature–composition diagram was constructed. From this diagram, the percentage of both components in a mixture of the two can be determined.

Cyclopropane and Benzene.—The technique was similar to that described for reactions between olefins and benzene.[1] Fractionation gave the following

Compound	B. p., °C.	n^{20}	Yields, %
Monopropylbenzene	154–157	1.4920	42
Dipropylbenzene	97–98 (16 mm.)	1.4928	20
Tripropylbenzene	130–131 (14 mm.)	1.4950	3

The sulfonamide of the monopropylbenzene melted at 99–105°, 99–105.2°. A mixed melting point with the corresponding derivative of pure isopropylbenzene was 80–92°. Thus cyclopropane gave the only normal propyl benzenes.

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[1] Simons and Archer, THIS JOURNAL, **60**, 2952 and 2953 (1938).

[2] Ipatieff and Grosse, *J. Org. Chem.*, **2**, 447 (1937).

[3] Farquharson and Sastri, *Trans. Faraday Soc.*, **33**, 1474 (1937).

[4] Grosse and Linn, *J. Org. Chem.*, **3**, 26 (1938).

Summary

Cyclopropane has been found to react with benzene catalyzed by hydrogen fluoride to give normal propylbenzenes in good yield. A possible mechanism for the reaction is postulated.

STATE COLLEGE, PENNA. RECEIVED SEPTEMBER 1, 1938

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Hydrogen Fluoride as a Condensing Agent. V. Reactions of Compounds Containing Oxygen and Reactions of Tertiary Halides with Olefins

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In the preceding papers of this series[1] the usefulness of hydrogen fluoride has been shown as a condensing agent for reactions between aromatic compounds and either unsaturated compounds or halides. That this reagent will promote many other reactions can now be shown. It appears that it catalyzes the same reactions that acidic reagents such as sulfuric acid catalyze and also the reactions that metallic halides such as aluminum chloride or boron trifluoride catalyze. For some reactions it is not only more convenient technically but also produces higher yields. There are reactions that hydrogen fluoride promotes that have not been reported using other reagents. One of these is a reaction between an aliphatic halide and an olefin. Two examples of this reaction are reported here in preliminary form. These are the reactions of tertiary butyl chloride with trimethylethylene and with cyclohexene.

The reactions of compounds containing oxygen are somewhat different from reactions of compounds that do not. Due to the peculiar properties of hydrogen fluoride, one cannot predict its effect in these reactions. To show the usefulness of hydrogen fluoride for them an account of the following reactions is included. Tertiary butyl alcohol has been caused to react with benzene to form tertiary butyl benzene, tertiary butyl chloride has reacted with phenol to form tertiary butyl phenol, and tertiary butyl chloride has been made to react with ethyl furoate. For these reactions larger quantities of hydrogen fluoride are required.

Many other types of reactions undoubtedly can be performed by means of hydrogen fluoride but the variety that has now been accomplished shows the general usefulness of this reagent in organic reactions. The reasons for its apparent uniqueness probably can be found in its physical and chemical properties. These have been summarized by Simons.[2] Despite its apparent weakness in aqueous solutions, it is a very powerful acidic substance. This property of donating protons makes it a useful reagent for organic reactions such as polymerizations and rearrangements in which a positive organic ion is the intermediate. The fact that the other halogen halides are insoluble in it accounts for the reactions in which a halogen halide is eliminated. Its unusual ability to form addition compounds, which is so evident in its numerous complex inorganic compounds, probably accounts for its usefulness in reactions involving aromatic compounds. A complex intermediate similar to those postulated for reactions using aluminum chloride may be the active agent. It is certainly much more soluble in benzene than would be expected from its high dielectric constant. It is readily eliminated during the course of many organic reactions in which not more than one fluorine atom is attached to the same carbon atom, not because the carbon fluoride bond is weak but because the energy of formation of hydrogen fluoride is so very high.

Experimental

The same techniques were used as previously described[1] with the following exceptions. Tertiary butyl alcohol was added at one time as it clogged the delivery tube if added slowly. Ethyl furoate was used in solution in carbon tetrachloride. Much larger quantities of hydrogen fluoride were required in reactions involving oxygen containing compounds, and the reactions required a longer time. The reaction of ethyl furoate required about one hundred and fifty hours.

Tertiary Butyl Chloride and Trimethylethylene.—Distillation of the reaction products gave a constant boiling fraction of refractive index 1.4279–1.4315. It boiled 63–65° at 19 mm. This product was definitely an olefin with physical properties corresponding to the expected nonenes. The remainder of the material boiled over a continuous range of temperatures both above and below the constant boiling fraction. Apparently many products

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[1] Simons and Archer, THIS JOURNAL, **60**, 2952 and 2953 (1938); Simons, Archer and Adams, *ibid.*, **60**, 2955 (1938).

[2] Simons, *Chem. Rev.*, **8**, 213 (1931).